10/530737

PCT/EP03/11388

The Patent Office
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Dated 26 September 2003

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Patents Act 1977
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1/77

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The Patent Office

Cardiff Road
Newport
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NP10 8QQ

1. Your reference

PPD 70036/GB/P

2. Patent application number
(The Patent Office will fill in this part)

0224316.0

18 OCT 2002

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SYNGENTA Participations AG
Intellectual Property Department
Schwarzwaldallee 215
CH-4058 Basel
SWITZERLAND

Patents ADP number *(if you know it)*

8029555001

If the applicant is a corporate body, give the country/state of its incorporation

SWITZERLAND

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Martin Keith Osborn
Intellectual Property Department
Syngenta Limited
Jealott's Hill International Research Centre
PO Box 3538
Bracknell, Berkshire, RG42 6YA
UNITED KINGDOM

Patents ADP number *(if you know it)*

8019945002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES (b)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	34
Claim(s)	02
Abstract	00
Drawing(s)	00

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Syngenta Participations AG

Signature J A Bowdich Date 18th October 2002

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Julie Anne BOWDICH = 01344 414102

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Notes

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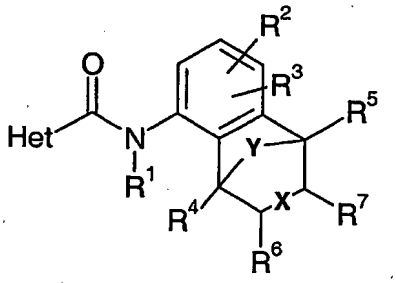
CHEMICAL COMPOUNDS

The present invention relates to novel tricyclic amine derivatives which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula (I):



(I)

where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^8, R^9 and R^{10};

X is a single or double bond;

Y is O, S, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$;

m is 0 or 1;

n is 0 or 1;

R^1 is hydrogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, $CH_2C{\equiv}CR^{18}$, $CH_2CR^{19}{=}CHR^{20}$, $CH{=}C{=}CH_2$ or COR^{21};

R^2 and R^3 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy or C_{1-4} haloalkoxy;

R^4, R^5, R^6 and R^7 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, hydroxymethyl, C_{1-4} alkoxymethyl, $C(O)CH_3$ or $C(O)OCH_3$;

R^8, R^9 and R^{10} are each, independently, hydrogen, halogen, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene or C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^8, R^9 and R^{10} is not hydrogen;

R^{11} is hydrogen, C_{1-4} alkyl, benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy), formyl, C(O)C_{1-4} alkyl, C_{1-4} alkoxycarbonyl or C_{1-4} alkoxy(C_{1-4})alkylene;

R^{12}, R^{13}, R^{14}, R^{15}, R^{16} and R^{17} are each, independently, hydrogen, C_{1-4} alkyl or C_{1-4} alkoxy;

R^{18}, R^{19} and R^{20} are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl or C_{1-4} alkoxy(C_{1-4})alkylene; and

R^{21} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene, C_{1-4} alkyl-S-(C_{1-4})alkylene, C_{1-4} alkoxy or aryl.

Halogen is fluoro, chloro, bromo or iodo; preferably fluoro, chloro or bromo.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, *neo*-pentyl, *n*-heptyl, 1,3-dimethylbutyl, 1,3-dimethylpentyl, 1-methyl-3-ethyl-butyl or 1,3,3-trimethylbutyl. Likewise, each alkylene moiety is a straight or branched chain.

Haloalkyl moieties are alkyl moieties which are substituted by one or more of the same or different halogen atoms and are, for example, CF_3, CF_2Cl, CHF_2, CH_2F, CCl_3, CF_3CH_2, CHF_2CH_2, CH_2FCH_2, CH_3CHF or CH_3CF_2.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains. The alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration.

Aryl includes phenyl, naphthyl, anthracyl, fluorenyl and indanyl but is preferably phenyl.

Het is preferably pyrrolyl, pyrazolyl, thiazolyl, oxazolyl, pyridinyl, pyrimidyl, pyridazinyl, 2,3-dihydro-[1,4]oxathiine-6-yl, oxazinyl, thiazinyl or triazinyl.

Het is more preferably pyrrolyl, pyrazolyl, thiazolyl, oxazolyl, pyridinyl or 2,3-dihydro-[1,4]oxathiine-yl.

Het is even more preferably pyrrolyl, pyrazolyl, thiazolyl or pyridinyl.

Het is most preferably pyrrolyl or pyrazolyl.

Preferably X is a single bond.

Preferably Y is O, S, $N(R^{11})$, CH_2, CH_2CH_2, $CH_2CH_2CH_2$, $C(CH_3)_2$, $CH(CH_3)$, $CH(C_2H_5)$, $C(CH_3)(C_2H_5)$, $CH(OCH_3)$ or $C(OCH_3)_2$.

More preferably Y is $N(R^{11})$, O, S, CH_2, CH_2CH_2, $CH_2CH_2CH_2$, $C(CH_3)_2$, $CH(CH_3)$ or $CH(C_2H_5)$.

Even more preferably Y is $N(R^{11})$, O, S, CH_2 or CH_2CH_2.

Still more preferably Y is O,CH_2 or $N(R^{11})$

Preferably n is 0.

Preferably m is 0.

Preferably R^1 is hydrogen, $CH_2C{\equiv}CR^{18}$, $CH{=}C{=}CH_2$ or COR^{21}.

More preferably R^1 is hydrogen, $CH_2C{\equiv}CH$, $CH{=}C{=}CH_2$ or $C(O)CH_3$.

Even more preferably R^1 is hydrogen, $CH_2C{\equiv}CH$ or $CH{=}C{=}CH_2$.

Most preferably R^1 is hydrogen.

Preferably R^2 is hydrogen, halogen or C_{1-4} alkyl.

More preferably R^2 is hydrogen or halogen.

Most preferably R^2 is hydrogen.

Preferably R^3 is hydrogen or methyl.

More preferably R^3 is hydrogen.

Preferably R^4 is hydrogen, C_{1-4} alkyl, halogen, C_{1-4} haloalkyl, C_{1-4} alkoxy, $C(O)CH_3$ or $C(O)OCH_3$.

More preferably R^4 is hydrogen, C_{1-2} alkyl, halogen, CF_3, methoxy, $C(O)CH_3$ or $C(O)OCH_3$.

Even more preferably R^4 is hydrogen, methyl, chlorine, CF_3 or methoxy.

Most preferably R^4 is hydrogen or methyl.

Preferably R^5 is hydrogen, C_{1-4} alkyl, halogen, C_{1-4} haloalkyl, C_{1-4} alkoxy, $C(O)CH_3$ or $C(O)OCH_3$.

More preferably R^5 is hydrogen, C_{1-2} alkyl, chlorine, CF_3, methoxy, $C(O)CH_3$ or $C(O)OCH_3$.

Most preferably R^5 is hydrogen or methyl.

Preferably R^6 is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy or $C(O)CH_3$.

More preferably R^6 is hydrogen, methyl, methoxy or $C(O)CH_3$.

Most preferably R^6 is hydrogen or methyl.

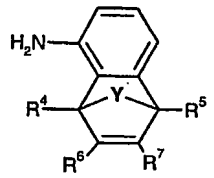
Preferably R^{20} is hydrogen, chloro, bromo, methyl or methoxy.

More preferably R^{20} is hydrogen, chloro or methyl.

Most preferably R^{20} is hydrogen.

Preferably R^{21} is hydrogen, methyl, $OC(CH_3)_3$ or CH_3OCH_2.

Compounds of formula (C):



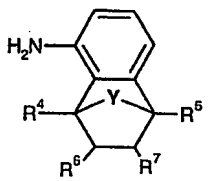
(C)

where Y, R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I) are useful as intermediates in the preparation of compounds of formula (I). Compounds of formula (C) are novel.

Therefore, in another aspect, the present invention provides a compound of formula (C) where Y, R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I).

Preferred compounds of formula (C) are those where R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I) and if at least one of R^4, R^5, R^6 and R^7 is $C(O)OCH_3$ then Y is as defined above for a compound of formula (I) but otherwise Y is NR^{11} where R^{11} is benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy), formyl, $C(O)C_{1-4}$ alkyl or C_{1-4} alkoxycarbonyl, preferably benzyl, formyl, $C(O)CH_3$ or $C(O)OC(CH_3)_3$.

Compounds of formula (D):



(D)

where Y, R^4, R^5, R^6 and R^7 are as defined above for a compound of formula (I) are also useful as intermediates in the preparation of compounds of formula (I). Compounds of formula (D) are novel.

1.24	H	H	H	H	$CH_2CH_2CH_2$
1.25	H	H	CH_3	CH_3	$C(CH_3)_2$
1.26	CH_3	CH_3	CH_3	CH_3	$C(CH_3)_2$
1.27	CH_3	H	CH_3	H	$C(CH_3)_2$
1.28	H	CH_3	H	CH_3	$C(CH_3)_2$
1.29	H	H	H	H	$C(CH_3)_2$
1.30	CH_3	CH_3	H	H	$C(CH_3)_2$
1.31	H	H	H	H	$C(OCH_3)_2$
1.32	H	H	H	H	S
1.33	CH_3	CH_3	H	H	S
1.34	H	H	CH_3	CH_3	S
1.35	OCH_3	OCH_3	H	H	S
1.36	H	CH_3	H	H	S
1.37	CH_3	H	H	H	S
1.38	CH_3	H	CH_3	H	S
1.39	H	CH_3	H	CH_3	S
1.40	H	OCH_3	H	H	S
1.41	OCH_3	H	H	H	S
1.42	CH_3	H	CH_3	CH_3	S
1.43	H	CH_3	CH_3	CH_3	S
1.44	H	H	CH_3	H	S
1.45	H	H	H	CH_3	S
1.46	H	H	OCH_3	H	S
1.47	H	H	H	OCH_3	S
1.48	H	H	H	H	$N(CH_3)$
1.49	CH_3	CH_3	H	H	$N(CH_3)$
1.50	H	H	H	H	$N(C_2H_5)$
1.51	H	H	H	H	NCH_2Ph
1.52	H	H	H	H	$NC(O)CH_3$
1.53	H	H	H	H	$NC(O)OC(CH_3)_3$
1.54	H	H	H	H	NH
1.55	H	H	H	H	NC(O)H
1.56	CH_3	CH_3	H	H	NC(O)H
1.57	CH_3	CH_3	H	H	NH
1.58	CH_3	CH_3	H	H	$NC(O)CH_3$
1.58	CH_3	CH_3	H	H	$NC(O)OC(CH_3)_3$
1.59	CH_3	CH_3	H	H	NCH_2Ph
1.60	Cl	Cl	H	H	O
1.61	H	H	H	H	$NC(O)OCH_3$
1.62	H	H	H	H	NCH_2-4-Cl-Ph
1.63	H	H	H	H	NCH_2-4-CH_3-Ph
1.64	H	H	H	H	NCH_2-3-Cl-Ph
1.65	H	H	H	H	NCH_2-3-CF_3-Ph
1.66	H	H	H	H	NCH_2-3-OCH_3-Ph

Table 2 provides 72 compounds of formula (D) wherein Y, R^4, R^5, R^6 and R^7 are as defined in Table 2.

Table 2

Cmpd. No.	R^4	R^5	R^6	R^7	Y
2.01	CH_3	CH_3	H	H	O
2.02	CH_3	H	H	H	O

2.03	H	CH_3	H	H	O
2.04	CH_3	CH_3	$C(O)CH_3$	H	O
2.05	CH_3	CH_3	H	$C(O)CH_3$	O
2.06	CH_3	$C(O)CH_3$	H	H	O
2.07	$C(O)CH_3$	CH_3	H	H	O
2.08	$C(O)OCH_3$	H	H	H	O
2.09	H	$C(O)OCH_3$	H	H	O
2.10	H	H	H	H	O
2.11	CF_3	CF_3	H	H	O
2.12	OCH_3	OCH_3	H	H	O
2.13	H	H	CH_3	CH_3	O
2.14	C_2H_5	C_2H_5	H	H	O
2.15	CH_3	H	CH_3	H	O
2.16	H	H	H	H	CH_2
2.17	CH_3	H	CH_3	H	CH_2
2.18	H	CH_3	H	CH_3	CH_2
2.19	CH_3	CH_3	CH_3	CH_3	CH_2
2.20	CH_3	CH_3	CH_3	CH_3	$CH(CH_3)$
2.21	H	H	H	H	$CH(CH_3)$
2.22	H	H	H	H	$CH(C_2H_5)$
2.23	H	H	H	H	CH_2CH_2
2.24	CH_3	CH_3	H	H	CH_2CH_2
2.25	H	H	CH_3	CH_3	CH_2CH_2
2.26	H	H	OCH_3	H	CH_2CH_2
2.27	H	H	H	OCH_3	CH_2CH_2
2.28	H	H	H	H	$CH_2CH_2CH_2$
2.29	H	H	CH_3	CH_3	$C(CH_3)_2$
2.30	CH_3	CH_3	CH_3	CH_3	$C(CH_3)_2$
2.31	CH_3	H	CH_3	H	$C(CH_3)_2$
2.32	H	CH_3	H	CH_3	$C(CH_3)_2$
2.33	CH_3	CH_3	CH_3	CH_3	$C(CH_3)(C_2H_5)$
2.34	H	H	H	H	$C(CH_3)_2$
2.35	CH_3	CH_3	H	H	$C(CH_3)_2$
2.36	H	H	H	H	$CH(OCH_3)$
2.37	H	H	H	H	S
2.38	CH_3	CH_3	H	H	S
2.39	H	H	CH_3	CH_3	S
2.40	OCH_3	OCH_3	H	H	S
2.41	H	CH_3	H	H	S
2.42	CH_3	H	H	H	S
2.43	CH_3	H	CH_3	H	S
2.44	H	CH_3	H	CH_3	S
2.45	H	OCH_3	H	H	S
2.46	OCH_3	H	H	H	S
2.47	CH_3	H	CH_3	CH_3	S
2.48	H	CH_3	CH_3	CH_3	S
2.49	H	H	CH_3	H	S
2.50	H	H	H	CH_3	S
2.51	H	H	OCH_3	H	S
2.52	H	H	H	OCH_3	S
2.53	H	H	H	H	$N(CH_3)$
2.54	CH_3	CH_3	H	H	$N(CH_3)$
2.55	H	H	H	H	$N(C_2H_5)$
2.56	H	H	H	H	NCH_2Ph
2.57	H	H	H	H	$NC(O)CH_3$

2.58	H	H	H	H	$NC(O)OC(CH_3)_3$
2.59	H	H	H	H	NH
2.60	Cl	Cl	H	H	O
2.61	H	H	H	H	NC(O)H
2.62	CH_3	CH_3	H	H	NC(O)H
2.63	CH_3	CH_3	H	H	NH
2.64	CH_3	CH_3	H	H	$NC(O)CH_3$
2.65	CH_3	CH_3	H	H	$NC(O)OC(CH_3)_3$
2.66	CH_3	CH_3	H	H	NCH_2Ph
2.67	H	H	H	H	$NC(O)OCH_3$
2.68	H	H	H	H	NCH_2-4-Cl-Ph
2.69	H	H	H	H	NCH_2-4-CH_3-Ph
2.70	H	H	H	H	NCH_2-3-Cl-Ph
2.71	H	H	H	H	NCH_2-3-CF_3-Ph
2.72	H	H	H	H	NCH_2-3-OCH_3-Ph

Table Z represents Table 3 [when Z is 3], Table 4 [when Z is 4], Table 5 [when Z is 5], Table 6 [when Z is 6] , Table 7 [when Z is 7], Table 8 [when Z is 8], Table 9 [when Z is 9], Table 10 [when Z is 10], Table 11 [when Z is 11], Table 12 [when Z is 12] , Table 13 [when Z is 13], Table 14 [when Z is 14], Table 15 [when Z is 15], Table 16 [when Z is 16], Table 17 [when Z is 17], Table 18 [when Z is 18], Table 19 [when Z is 19], Table 20 [when Z is 20], Table 21 [when Z is 21], Table 22 [when Z is 22], Table 23 [when Z is 23], Table 24 [when Z is 24], Table 25 [when Z is 25], Table 26 [when Z is 26], Table 27 [when Z is 27], Table 28 [when Z is 28] and represents Table 29 [when Z is 29].

Table Z

Cpd. No.	R^1	R^4	R^5	R^6	R^7	X — single bond = double bond	Y
Z.001	H	CH_3	CH_3	H	H	=	O
Z.002	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	=	O
Z.003	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	=	O
Z.004	$C(O)CH_3$	CH_3	CH_3	H	H	=	O
Z.005	H	CH_3	H	H	H	=	O
Z.006	H	H	CH_3	H	H	=	O
Z.007	H	CH_3	CH_3	$C(O)CH_3$	H	=	O
Z.008	H	CH_3	CH_3	H	$C(O)CH_3$	=	O
Z.009	H	CH_3	$C(O)CH_3$	H	H	=	O
Z.010	H	$C(O)CH_3$	CH_3	H	H	=	O
Z.011	H	$COOCH_3$	H	H	H	=	O
Z.012	H	H	$COOCH_3$	H	H	=	O
Z.013	H	H	H	H	H	=	O
Z.014	$CH_2C{\equiv}CH$	H	H	H	H	=	O
Z.015	$CH{=}C{=}CH_2$	H	H	H	H	=	O
Z.016	$COCH_3$	H	H	H	H	=	O
Z.017	H	CF_3	CF_3	H	H	=	O
Z.018	H	OCH_3	OCH_3	H	H	=	O

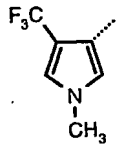
Z.019	H	H	H	CH_3	CH_3	=	O
Z.020	H	C_2H_5	C_2H_5	H	H	=	O
Z.021	H	CH3	H	CH_3	H	=	O
Z.022	H	H	CH3	H	CH_3	=	O
Z.023	H	CH_3	CH_3	H	H	–	O
Z.024	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	–	O
Z.025	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	–	O
Z.026	$COCH_3$	CH_3	CH_3	H	H	–	O
Z.027	H	CH_3	H	H	H	–	O
Z.028	H	H	CH_3	H	H	–	O
Z.029	H	CH_3	CH_3	$C(O)CH_3$	H	–	O
Z.030	H	CH_3	CH_3	H	$C(O)CH_3$	–	O
Z.031	H	CH_3	C(O)CH3	H	H	–	O
Z.032	H	$C(O)CH_3$	CH_3	H	H	–	O
Z.033	H	$COOCH_3$	H	H	H	–	O
Z.034	H	H	$COOCH_3$	H	H	–	O
Z.035	H	H	H	H	H	–	O
Z.036	$CH_2C{\equiv}CH$	H	H	H	H	–	O
Z.037	$CH{=}C{=}CH_2$	H	H	H	H	–	O
Z.038	$COCH_3$	H	H	H	H	–	O
Z.039	H	H	H	H	H	–	O
Z.040	H	CF_3	CF_3	H	H	–	O
Z.041	H	OCH_3	OCH_3	H	H	–	O
Z.042	H	H	H	CH_3	CH_3	–	O
Z.043	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	O
Z.044	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	O
Z.045	$COCH_3$	H	H	CH_3	CH_3	–	O
Z.046	H	C_2H_5	C_2H_5	H	H	–	O
Z.047	H	CH_3	H	CH_3	H	–	O
Z.048	H	H	H	H	H	–	CH_2
Z.049	$CH_2C{\equiv}CH$	H	H	H	H	–	CH_2
Z.050	$CH{=}C{=}CH_2$	H	H	H	H	–	CH_2
Z.051	$COCH_3$	H	H	H	H	–	CH_2
Z.052	H	H	H	H	H	=	CH_2
Z.053	$CH_2C{\equiv}CH$	H	H	H	H	=	CH_2
Z.054	$CH{=}C{=}CH_2$	H	H	H	H	=	CH_2
Z.055	$COCH_3$	H	H	H	H	=	CH_2
Z.056	H	CH_3	H	CH_3	H	–	CH_2
Z.057	H	CH_3	H	CH_3	H	=	CH_2
Z.058	H	H	CH_3	H	CH_3	–	CH_2
Z.059	H	H	CH_3	H	CH_3	=	CH_2
Z.060	H	CH_3	CH_3	CH_3	CH_3	=	CH_2
Z.061	H	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.062	$CH_2C{\equiv}CH$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.063	$CH{=}C{=}CH_2$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.064	$COCH_3$	CH_3	CH_3	CH_3	CH_3	–	CH_2
Z.065	H	CH_3	CH_3	CH_3	CH_3	=	$CH(CH_3)$
Z.066	H	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$
Z.067	$CH_2C{\equiv}CH$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$
Z.068	$CH{=}C{=}CH_2$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$
Z.069	$COCH_3$	CH_3	CH_3	CH_3	CH_3	–	$CH(CH_3)$
Z.070	H	H	H	H	H	=	$CH(CH_3)$
Z.071	H	H	H	H	H	–	$CH(CH_3)$
Z.072	$CH_2C{\equiv}CH$	H	H	H	H	–	$CH(CH_3)$
Z.073	$CH{=}C{=}CH_2$	H	H	H	H	–	$CH(CH_3)$

Z.074	$COCH_3$	H	H	H	H	–	$CH(CH_3)$
Z.075	H	H	H	H	H	–	$CH(C_2H_5)$
Z.076	H	H	H	H	H	–	CH_2CH_2
Z.077	$CH_2C{\equiv}CH$	H	H	H	H	–	CH_2CH_2
Z.078	$CH{=}C{=}CH_2$	H	H	H	H	–	CH_2CH_2
Z.079	$COCH_3$	H	H	H	H	–	CH_2CH_2
Z.080	H	CH_3	CH_3	H	H	=	CH_2CH_2
Z.081	H	CH_3	CH_3	H	H	–	CH_2CH_2
Z.082	H	H	H	CH_3	CH_3	=	CH_2CH_2
Z.083	H	H	H	CH_3	CH_3	–	CH_2CH_2
Z.084	H	H	H	OCH_3	H	–	CH_2CH_2
Z.085	H	H	H	H	OCH_3	–	CH_2CH_2
Z.086	H	H	H	H	H	–	$CH_2CH_2CH_2$
Z.087	H	H	H	H	H	=	$CH_2CH_2CH_2$
Z.088	H	H	H	CH_3	CH_3	=	$C(CH_3)_2$
Z.089	H	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.090	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.091	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.092	$COCH_3$	H	H	CH_3	CH_3	–	$C(CH_3)_2$
Z.093	H	CH_3	CH_3	CH_3	CH_3	=	$C(CH_3)_2$
Z.094	H	CH_3	CH_3	CH_3	CH_3	–	$C(CH_3)_2$
Z.095	H	CH_3	H	CH_3	H	–	$C(CH_3)_2$
Z.096	H	H	CH_3	H	CH_3	–	$C(CH_3)_2$
Z.097	H	CH_3	H	CH_3	H	=	$C(CH_3)_2$
Z.098	H	H	CH_3	H	CH_3	=	$C(CH_3)_2$
Z.099	H	CH_3	CH_3	CH_3	CH_3	–	$C(CH_3)(C_2H_5)$
Z.100	H	H	H	H	H	–	$C(CH_3)_2$
Z.101	$CH_2C{\equiv}CH$	H	H	H	H	–	$C(CH_3)_2$
Z.102	H	H	H	H	H	=	$C(CH_3)_2$
Z.103	H	CH_3	CH_3	H	H	–	$C(CH_3)_2$
Z.104	H	CH_3	CH_3	H	H	=	$C(CH_3)_2$
Z.105	H	H	H	H	H	=	$C(OCH_3)_2$
Z.106	H	H	H	H	H	–	$CH(OCH_3)$
Z.107	H	H	H	H	H	=	S
Z.108	$CH_2C{\equiv}CH$	H	H	H	H	=	S
Z.109	$CH{=}C{=}CH_2$	H	H	H	H	=	S
Z.110	$COCH_3$	H	H	H	H	=	S
Z.111	H	H	H	H	H	–	S
Z.112	$CH_2C{\equiv}CH$	H	H	H	H	–	S
Z.113	$CH{=}C{=}CH_2$	H	H	H	H	–	S
Z.114	$COCH_3$	H	H	H	H	–	S
Z.115	H	CH_3	CH_3	H	H	=	S
Z.116	H	CH_3	CH_3	H	H	–	S
Z.117	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	–	S
Z.118	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	–	S
Z.119	$COCH_3$	CH_3	CH_3	H	H	–	S
Z.120	H	H	H	CH_3	CH_3	=	S
Z.121	H	H	H	CH_3	CH_3	–	S
Z.122	$CH_2C{\equiv}CH$	H	H	CH_3	CH_3	–	S
Z.123	$CH{=}C{=}CH_2$	H	H	CH_3	CH_3	–	S
Z.124	$COCH_3$	H	H	CH_3	CH_3	–	S
Z.125	H	OCH_3	OCH_3	H	H	=	S
Z.126	H	OCH_3	OCH_3	H	H	–	S
Z.127	H	H	CH_3	H	H	=	S
Z.128	H	H	CH_3	H	H	–	S

Z.129	H	CH_3	H	H	H	=	S
Z.130	H	CH_3	H	H	H	–	S
Z.131	H	CH_3	H	CH_3	H	=	S
Z.132	H	CH_3	H	CH_3	H	–	S
Z.133	H	H	CH_3	H	CH_3	=	S
Z.134	H	H	CH_3	H	CH_3	–	S
Z.135	H	H	OCH_3	H	H	=	S
Z.136	H	H	OCH_3	H	H	–	S
Z.137	H	OCH_3	H	H	H	=	S
Z.138	H	OCH_3	H	H	H	–	S
Z.139	H	CH_3	H	CH_3	CH_3	=	S
Z.140	H	CH_3	H	CH_3	CH_3	–	S
Z.141	H	H	CH_3	CH_3	CH_3	=	S
Z.142	H	H	CH_3	CH_3	CH_3	–	S
Z.143	H	H	H	CH_3	H	=	S
Z.144	H	H	H	CH_3	H	–	S
Z.145	H	H	H	H	CH_3	=	S
Z.146	H	H	H	H	CH_3	–	S
Z.147	H	H	H	OCH_3	H	=	S
Z.148	H	H	H	OCH_3	H	–	S
Z.149	H	H	H	H	OCH_3	=	S
Z.150	H	H	H	H	OCH_3	–	S
Z.151	H	H	H	H	H	=	$N(CH_3)$
Z.152	H	H	H	H	H	–	$N(CH_3)$
Z.153	$CH_2C{\equiv}CH$	H	H	H	H	–	$N(CH_3)$
Z.154	$CH{=}C{=}CH_2$	H	H	H	H	–	$N(CH_3)$
Z.155	$COCH_3$	H	H	H	H	–	$N(CH_3)$
Z.156	H	CH_3	CH_3	H	H	=	$N(CH_3)$
Z.157	H	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.158	$CH_2C{\equiv}CH$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.159	$CH{=}C{=}CH_2$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.160	$COCH_3$	CH_3	CH_3	H	H	–	$N(CH_3)$
Z.161	H	H	H	H	H	=	$N(C_2H_5)$
Z.162	H	H	H	H	H	–	$N(C_2H_5)$
Z.163	H	H	H	H	H	=	NCH_2Ph
Z.164	H	H	H	H	H	–	NCH_2Ph
Z.165	H	H	H	H	H	=	$NC(O)CH_3$
Z.166	H	H	H	H	H	–	$NC(O)CH_3$
Z.167	H	H	H	H	H	=	$NC(O)OC(CH_3)_3$
Z.168	H	H	H	H	H	–	$NC(O)OC(CH_3)_3$
Z.169	H	H	H	H	H	=	NH
Z.170	H	H	H	H	H	–	NH
Z.171	H	H	H	H	H	=	NC(O)H
Z.172	H	H	H	H	H	–	NC(O)H
Z.173	H	CH_3	CH_3	H	H	=	NCH_2Ph
Z.174	H	CH_3	CH_3	H	H	–	NCH_2Ph
Z.175	H	CH_3	CH_3	H	H	=	$NC(O)CH_3$
Z.176	H	CH_3	CH_3	H	H	–	$NC(O)CH_3$
Z.177	H	CH_3	CH_3	H	H	=	$NC(O)OC(CH_3)_3$
Z.178	H	CH_3	CH_3	H	H	–	$NC(O)OC(CH_3)_3$
Z.179	H	CH_3	CH_3	H	H	=	NH
Z.180	H	CH_3	CH_3	H	H	–	NH
Z.181	H	CH_3	CH_3	H	H	=	NC(O)H
Z.182	H	CH_3	CH_3	H	H	–	NC(O)H
Z.183	H	H	H	H	H	H	$NC(O)OCH_3$

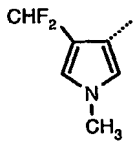
Z.184	H	H	H	H	H	H	NCH_2-4-Cl-Ph
Z.185	H	H	H	H	H	H	NCH_2-4-CH_3-Ph
Z.186	H	H	H	H	H	H	NCH_2-3-Cl-Ph
Z.187	H	H	H	H	H	H	NCH_2-3-CF_3-Ph
Z.188	H	H	H	H	H	H	NCH_2-3-OCH_3-Ph

Table 3 provides 188 compounds of formula (I) where Het is



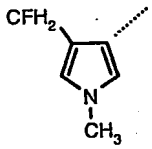
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 3.

Table 4 provides 188 compounds of formula (I) where Het is



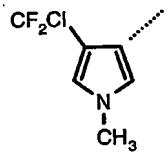
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 4.

Table 5 provides 188 compounds of formula (I) where Het is



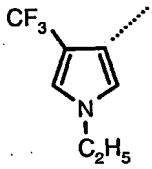
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 5.

Table 6 provides 188 compounds of formula (I) where Het is



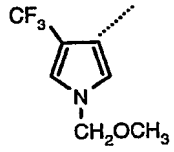
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 6.

Table 7 provides 188 compounds of formula (I) where Het is



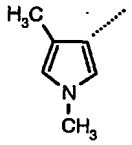
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 7.

Table 8 provides 188 compounds of formula (I) where Het is



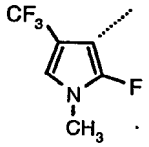
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 8.

Table 9 provides 188 compounds of formula (I) where Het is



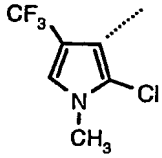
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 9.

Table 10 provides 188 compounds of formula (I) where Het is



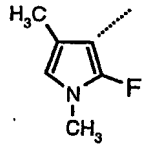
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 10.

Table 11 provides 188 compounds of formula (I) where Het is



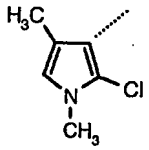
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 11.

Table 12 provides 188 compounds of formula (I) where Het is



R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 12.

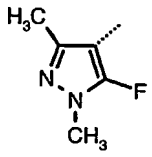
Table 13 provides 188 compounds of formula (I) where Het is



R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 13.

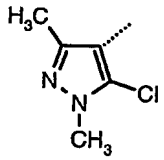
Table 14 provides 188 compounds of formula (I) where Het is

Table 20 provides 188 compounds of formula (I) where Het is



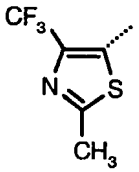
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 20.

Table 21 provides 188 compounds of formula (I) where Het is



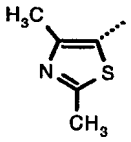
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 21.

Table 22 provides 188 compounds of formula (I) where Het is



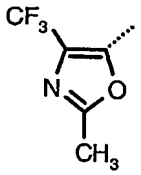
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 22.

Table 23 provides 188 compounds of formula (I) where Het is



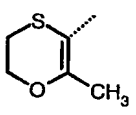
R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 23.

Table 24 provides 188 compounds of formula (I) where Het is



R^2 and R^3 are both hydrogen; and X, Y, R^1, R^4, R^5, R^6 and R^7 are as defined in Table 24.

Table 25 provides 188 compounds of formula (I) where Het is



for example, [$CDCl_3$ / d_6-DMSO]), (no attempt is made to list all characterising data in all cases) for compounds of Tables 1 to 29.

Table 30

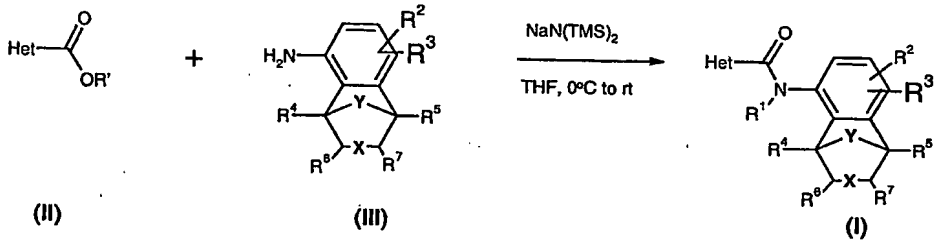
Compund No.	m.p (/°C)	NMR proton shifts (/ppm) ($CDCl_3$ unless otherwise stated)
1.01	92-96	6.85 and 6.7(two m,2 x 2H), 6.47(t,1H), ca.5-3(br.,exchangeable with D_2O, 2H), 2.07(s,3H), 1.85(s,3H).
1.10	121-124	
2.01	92-93	7.05(t,1H), 6.7(t,2H), ca.5(brd,exchangeable with D_2O,2H), 2.0(s,3H), 1.9(m,2H), 1.8(s,3H), 1.7(m,1H), 1.5(m,1H).
2.02	92-93	
2.03	112-114	
2.10	75-76	
2.16	yellow oil	6.90(dd (~t), J_1= 7.3 Hz, J_2 = 8.2 Hz, 1H), 6.65(d,J=7.3Hz,1H), 6.46(d,J = 8.2 Hz,1H), 3.46 (br.,exchangeable with D_2O,2H), 3.35(br.s,1H), 3.31(br.s,1H), 1.87(m,2H), 1.70(m,1H), 1.50(m,1H), 1.18(m,1H).
2.58	89-90	6.94(dd (~t), J_1= 7.3Hz, J_2= 7.9Hz,1H), 6.68(d,J=7.3Hz,1H), 6.49 (d, J= 7.9Hz,1H), 5.11(br,1H), 5.04(br,1H), 3.5-3.0(br,2H, exchangeable with D_2O), 2.07(m,2H), 1.40(s,9H), 1.30(m,2H).
2.59	oil	6.91(dd (~t), J_1= 7.3Hz, J_2= 7.9Hz,1H), 6.66(d,J=7.3Hz,1H), 6.44(d, J=7.9Hz,1H), 4.55(d, J=~1 Hz,1H)), 4.48(d,J=~1 Hz,1H), 4.0-3.0(br, exchangeable with D_2O, H), 2.02(m,2H), 1.25(m,2H).
3.001	150-154	
3.002	163-165	
3.023	129-133 [as a mixture of atropisomers]	7.62(br), 7.44(d,J ~ 1 Hz), 7.32(d,J ~ 1 Hz), 7.2(m), 7.0(m); these signals account for 6 protons. Further signals at 3.7(s,3H), 1.84(s,3H), 1.82(s,3H), 2.0-1.5(m,4H).
3.024	172-176	7.5–7.0(m) and 6.8(br.s) accounting for 5H, 5.7–4.8 (two sets of AB systems,2H), 4.1(m,1H), 3.35 and 3.3(two s, accounting for 3H), 1.85, 1.75, 1.70(three s, accounting for 6H), 2.0–1.4(m,4H).
3.027	amorphous solid	7.60 br.s,1H), 7.34(br.s,1H), 7.22-7.07(m,3H), 7.01(br.s,1H), 5.27(d,1H), 3.71(s,3H), 2.19(m,1H), 1.91(m,1H), 1.83(s,3H), 1.71(m,1H), 1.49(m,1H).
3.028	amorphous solid	7.68(br.,1H), 7.53(d,1H), 7.37(br.s,1H), 7.17(t,1H), 7.00(br.s,1H), 6.96(d,1H), 5.39(d,1H), 3.70(s,3H), 2.25(m,1H), 1.83(s,3H), 1.83-1.66(m,2H), 1.48(m,1H).
3.035	amorphous solid	

24.048	viscous oil	7.85(br.,1H), 7.72(d,1H), 7.12–7.02(m,2H), 3.43(br.s,1H), 3.40(br.s,1H), 2.63(s,3H), 1.93(m,2H), 1.78(m,1H), 1.55(m,1H), 1.23(m,2H).
29.048	158-160	
29.052	151-152	

The compounds according to formula (I) may be prepared according to the following reaction schemes.

Preparation of a compound of formula (I)

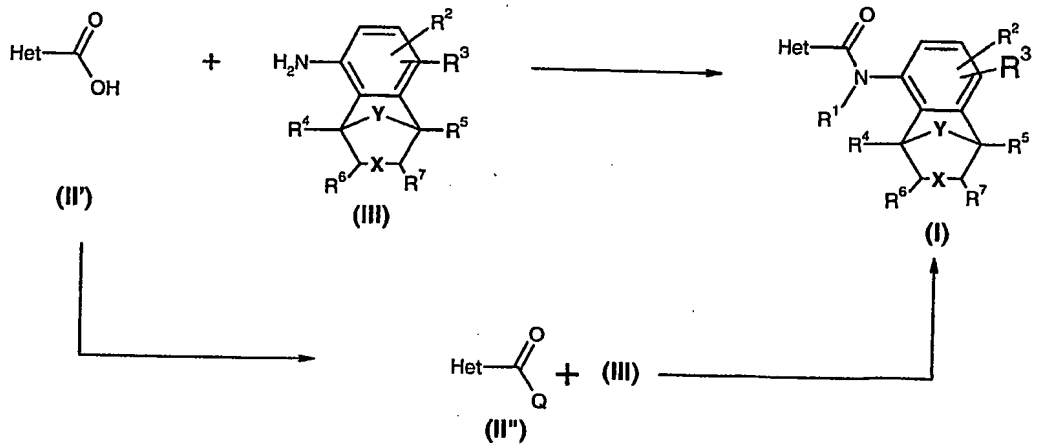
Scheme 1



(II) (III) (I)

A compound of formula (I) [where R^1 is hydrogen; and Het, R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] may be synthesized by reacting a compound of (II) [where Het is as defined above for a compound of formula (I) and R' is $C_{1\text{-}5}$ alkyl] with an aniline of formula (III) [where R^2, R^3, R^4, R^5, R^6, R^7, X and Y are as defined above for a compound of formula (I)] in the presence of $NaN(TMS)_2$ at -10°C to ambient temperature, preferably in dry THF, as described by *J.Wang et al., Synlett*, 2001, 1485.

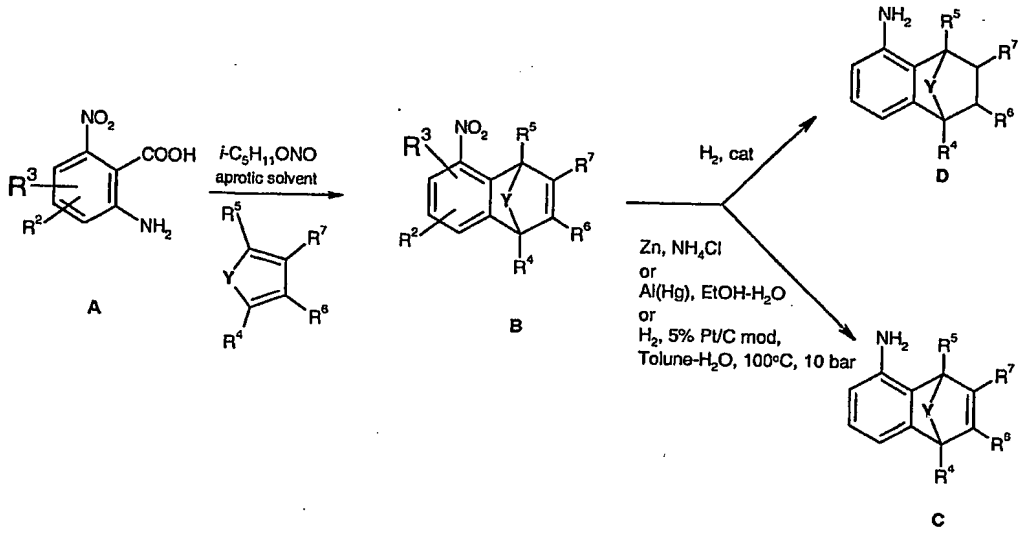
Scheme 2



Heterocyclic acids and esters [that is, compounds of formula (II') or (II)] are generally known from the literature or may be synthesized according to known methods.

Ortho-substituted aminobenzonorbonenes (including homologues) of formula (C) or (D) (scheme 4) may be accomplished through *Diels-Alder* addition of an *in situ* generated benzyne [starting from a 6-nitroanthranilic acid of formula (A), for example as described by L.Paquette et al, J. Amer. Chem. Soc. 99, 3734 (1977)] to a 5-7 membered cyclic 1,4-diene to give a nitro-benzonorbornadiene of formula (B). Suitable aprotic solvents for this step include ethyl acetate, dichloromethane, acetone, THF and dimethoxyethane. Reaction temperatures range from room temperature to 100°C, preferably 40-80°C. Subsequent selective reduction of the nitro-group in a compound of formula (B) to give an amino-benzonorbornadiene of formula (C) requires mild conditions [for example, either metallic zinc in the presence of ammonium chloride, or aluminium amalgam]. Both methods work in protic solvents such as ethanol, water or mixtures thereof. Alternatively a compound of formula (C) may also be obtained from a compound of formula (B) by catalytic hydrogen reduction with a modified 5% Pt/C catalyst at elevated pressure (~10bar) and elevated temperature (~100°C) in toluene-water. Catalytic reduction under standard conditions (for example 5% Pd/C or Ra/Ni) in a solvent [such as methanol, ethanol, THF or ethyl acetate] reduces both the nitro-group and the double bond to furnish a benzonorbornene of formula (D). Preferred reaction conditions are ambient temperature and normal pressure.

Scheme 4



Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula (I) are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO97/33890.

The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with

cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

A preferred method of applying a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, for example in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

under initial ice cooling with oxalyl chloride (0.805g; 1.2eq.) for 2hours. Within 15minutes, the reaction mixture was then added dropwise to a solution of 1,8-dimethyl-11-oxa-tricyclo[6.2.1.0*2,7*]undeca-2,4,6-trien-3-ylamine (Compound No. 2.01; see preparation above) (1.0g; 5.284mmol) and triethylamine (1.07g; 10.57mmol) in 20ml dichloromethane under cooling (3-7°C) with subsequent stirring at ambient temperature for 3¼hours. The reaction mixture was then poured on to ice water and extracted with dichloromethane to give 2.26g of crude product. Purification on silica gel in ethyl acetate-hexane (1:1) followed by trituration with ether-hexane furnished a solid (1.14g; 59%) as a mixture of atropisomers.

EXAMPLE 5

This Example illustrates the preparation of Compound No.3.024.

A suspension of NaH (0.107g; 60% oil dispersion, ~2.7mmol) in DMF (5ml) was reacted with a solution of 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid(1,8-dimethyl-11-oxa-tricyclo[6.2.1.0*2,7*]undeca-2,4,6-trien-3-yl)-amide (Compound No. 3.023; see preparation above) (0.65g; 1.784mmol) in 5ml DMF at 10-15°C for 30minutes. 3-Bromo-1-propyne (0.276g; 2.32mmol) was added and the mixture was further reacted overnight at ambient temperature. After aqueous work up with ice water and ethyl acetate and purification on silica gel 0.36g (50%) of the desired product as a mixture of atropisomers were obtained.

FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable Concentrates, Solutions, Granules, Dusts and Wettable Powders are described in WO97/33890.

BIOLOGICAL EXAMPLES: FUNGICIDAL ACTIONS

Example B-1: Action against Puccinia recondita / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. the plants are kept in a

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the grape plants are inoculated by spraying a spore suspension ($1x10^6$ conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds 14.048, 15.048, 3.028 and 15.027 each show good activity in this test (<50% disease incidence).

Example B-6: Action against Botrytis cinerea / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($1x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

Compounds 3.048, 3.052, 14.052, 15.048 and 15.023 each exhibit good efficacy (<50% disease incidence).

Example B-7: Action against Septoria nodorum / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($5x10^5$conidia/ml) on the test plants. After an incubation period of 1 day at 20°C and 95%r.h. the plants are kept for 10 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation.

Compounds 3.002, 3.048, 14.048 and 15.048 each show good activity in this test (<50% disease incidence).

Example B-8: Action against Helminthosporium teres / barley (Net blotch on barley)

1 week old barley plants cv. Regina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the barley plants are inoculated by spraying a spore suspension ($3x10^4$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds 3.023, 14.023, 3.048, 14.048, 15.048, 3.027, 15.023, 15.027 and 15.028 each show good activity in this test (<20% disease incidence).

Example B-9: Action against Alternaria solani / tomato (Early blight on tomatoes)

are then incubated for 11days at ca.10-18° C and 100%r.h. with a daily light period of 14hours. The evaluation is made by assessing the degree of disease occurrence in the form of brown lesions on the roots.

Compounds 14.024, 15.048, 20.048, 14.027, 24.048 and 3.035 each show good activity in this test (<50% disease incidence).

Example B-13: Action Gaeumannomyces graminis / wheat (Take-all on wheat) (pouch test)

A defined amount of mycelium of G. graminis is mixed with water. The formulated test compound (0.002% active ingredient) is added to the mycelium suspension. The mixture is applied into a pouch which was previously equipped with a filter paper. After the application wheat seeds (cv.Orestis) are sown into the upper fault of the filter paper. The prepared pouches are then incubated for 14days at 18°C/16°C (day/night) and 80%r.h. with a daily light period of 14hours. The evaluation is made by assessing the degree of root browning.

Compounds 15.048, 20.048, 21.048, 15.028 and 15.052 each show good activity in this test (<50% disease incidence).

Example B-14: Action against Puccinia recondita / wheat (Brownrust on wheat) (Pouch test)

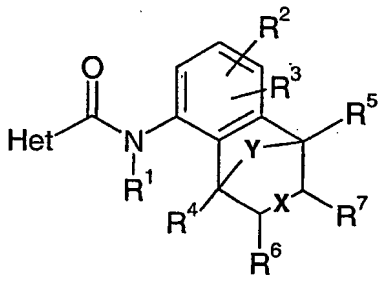
Formulated test compound (0.002% active ingredient) is applied into a pouch which was previously equipped with a filter paper. After the application wheat seeds (cv.Arina) are sown into the upper fault of the filter paper. The prepared pouches are then incubated at 23°C/18°C (day/night) and 80%r.h. One week after sowing, the wheat plants were inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 1day at 23°C and 95%r.h. the plants were kept for 9days at 20°C/18°C (day/night) and 80%r.h . The disease incidence was assessed 10days after inoculation. The efficacy of each test compound is used as an indicator for systemic activity.

Compounds 14.024, 3.002, 14.002, 15.048, 20.048, 3.027, 22.048, 15.023, 15.027, 15.028, 3.035, 14.035 and 15.035 each show good activity in this test (<50% disease incidence).

Example B-15: Action against Rhizoctonia solani / rice (Sheath blight on rice) (Pouch test)

CLAIMS

1. A compound of formula (I)):



(I)

where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^8, R^9 and R^{10};

X is a single or double bond;

Y is O, S, $N(R^{11})$ or $(CR^{12}R^{13})(CR^{14}R^{15})_m(CR^{16}R^{17})_n$;

m is 0 or 1;

n is 0 or 1;

R^1 is hydrogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, $CH_2C{\equiv}C$-R^{18}, $CH_2CR^{19}{=}CHR^{20}$, $CH{=}C{=}CH_2$ or COR^{21};

R^2 and R^3 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} alkoxy or C_{1-4} haloalkoxy;

R^4, R^5, R^6 and R^7 are each, independently, hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy, C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, $C(O)CH_3$ or $C(O)OCH_3$;

R^8, R^9 and R^{10} are each, independently, hydrogen, halogen, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene or C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^8, R^9 and R^{10} is not hydrogen;

R^{11} is hydrogen, C_{1-4} alkyl, benzyl (in which the phenyl group is optionally substituted with up to three substituents, each independently selected from halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy), formyl, $C(O)C_{1-4}$ alkyl, C_{1-4} alkoxycarbonyl or C_{1-4} alkoxy(C_{1-4})alkylene;